



PROCESS FOR PRODUCTION OF NEW CATALYSTS USING AN EVOLUTIONARY PROCESS

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates to a process which permits an improved production and selection of catalysts according to an evolutionary process.

Description of the Related Art

[0002] German Patent DE 198 43 242.9 describes a method of producing active and or selective catalysts from inorganic and organometallic solids or mixtures thereof, whereby potentially catalytic active individual components are first identified in the evolutionary search and optimization method, and by their randomized qualitative and quantitative combination with numerous materials, a first generation of mixed materials is produced and then subjected to catalytic testing. In addition, it has already been reported that to produce a new generation according to the principles of mutations and crossing, the best materials of the first generation are selected. This procedure has then been used further for all subsequent generations. However, it has been found that although this procedure leads to catalysts containing catalytically active components, other original components are already removed from the remaining selection process in the first or subsequent generations despite the fact that they could be necessary for an optimum catalyst.

SUMMARY OF THE INVENTION

[0003] The object of this invention is to further improve upon the evolutionary selection strategy and to include catalyst components and performance parameters.

[0004] According to this invention, the range of available catalyst components in evolutionary selection, where choices

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[0005] This requires a stronger representation of mixed materials having a good catalytic efficiency in the following generations but at the same time retaining at first the mixed materials that are not excellent but whose individual components might be quite beneficial in other combinations, in order to thereby review their possibly positive effect in the following generations. Only when it is found in the evolutionary optimization process that these individual components do not contribute to an improvement in the catalytic materials are they ruled out during the further evolutionary process.

[0007] Therefore, according to this invention, the process for producing active heterogeneous catalysts of an inorganic nature through selection of solid materials having various compositions and through restructuring of the original catalysts and subsequent catalyst generations by means of stochastic methods and determination of the performance parameters of the respective catalyst generation and selection of the mixed catalysts of one or more catalyst generations is characterized in that the restructuring, if based on the principle of crossing, takes place in such a way that a mixed catalyst is randomly selected from a generation of catalysts by means of a numerical random generator with a uniform

distribution (e.g., by means of the program code G05DYF of the NAG Library [NAG FORTRAN Workstation Library, NAG Group Ltd., 1986]), and a second mixed catalyst is selected from the same generation with the probability W by means of numerical random generators with a uniform distribution (for example, by means of a combination of the program codes G05DYF and G05DZF of the NAG Library [NAG FORTRAN Workstation Library, NAG Group Ltd., 1986]), where the following formulation is selected by W_i

$$W_i = \frac{\left(\sum_{j=1}^n j \right) - i}{\left(\sum_{j=1}^n j \right)}$$

[0008] where i and j denote the ranking of the catalysts of one generation, ranked according to decreasing catalytic activity, and n is the number of catalysts in one generation,

[0009] and then from the two mixed catalysts to be crossed, at least one individual component which is present in only one of the two catalysts is selected according to the random principle by means of a numerical random generator with a uniform distribution (for example, by means of the program code G05DYF of the NAG Library [NAG FORTRAN Workstation Library, NAG Group Ltd., 1986]) and two new catalyst compositions of the next generation are defined in such a way that the selected component is then added to the catalyst which did not contain this component in the preceding generation, while the component in the catalyst containing it originally is omitted,

[00010] and

[00011] the restructuring of a catalyst of the next generation, when it is based on the principle of mutation, takes places in such a manner

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[00012] that first a mixed catalyst is randomly selected from a catalyst generation by means of a numerical random generator with a uniform distribution (for example, by means of the program code G05DYF of the NAG Library [NAG FORTRAN Workstation Library, NAG Group Ltd., 1986]), and then a single component is selected according to the random principle by means of a numerical random generator with a uniform distribution (for example, by means of the program code G05DYF of the NAG Library [NAG FORTRAN Workstation Library, NAG Group Ltd., 1986]), and if this individual component is already contained in the mixed catalyst, it is removed or, if it has not yet been contained in this catalyst, it is added to it.

[00013] This type of crossing and mutation is carried out until the mixed catalysts produced in this way no longer show any definite improvement within one generation. In this way it is possible to allow individual components to participate in the process of selection and testing of the properties of the newly structured mixed materials for a longer period of time and to cull them out only when no further improvement in properties with respect to catalytic activity and/or selectivity is clearly discernible any longer in the corresponding mixed catalysts.

[00014] All the chemical elements and support components for catalysts which are also listed in German Patent Application 19843242.9 and International Patent 00/15341, to which reference is herewith made explicitly, may be used as catalytic components, i.e., Li, Na, K, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce, Nd, or as catalytic supports, the oxides, carbonates, carbides, nitrides, borides of Mg, Ca, Sr, Ba, La, Zr, Ce, Al, Si or mixtures thereof.

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[00021] As explained above, the evolutionary strategies such as crossing and mutation (implemented in actual practice by using numerical random generators with a uniform distribution B in contrast with random generators with a logarithmic normal distribution, a Weibull distribution, a Candy distribution, etc.) are implemented in this way, despite the fact that extraction and cubing are also equivalent stochastic methods. In the case of numerical random generators, the program codes G05CAF, G05DYF, G05DZF or G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986) of a

numerical random generator are used to advantage.

[00022] Random generators which are freely available on the Internet or those available commercially as software such as "Numerical Recipes in FORTRAN, PASCAL or C" from the Cambridge University Press, or IMSL libraries of the FORTRAN compilers DIGITAL Visual Fortran Professional Edition may also be used.

[00023] Thus, for example, by using such methods, several catalyst components can be selected and their corresponding molar substance amounts exchanged among the previously selected catalysts components (crossing). In this way, it is also possible to bring about an exchange of the individual catalyst components themselves by means of crossing for the use of quantitative amounts which are altered from a finite value to zero or from zero to a finite value, thus obtaining on the whole a new composition of a catalyst of the new generation. However, a catalyst component selected by random generator, for example, can also be increased or reduced (mutation) by multiplying by factors that are either freely selected or are randomly determined from the quantity of real numbers between 0 and 10,000, so that although the new catalyst of the next catalyst generation contains the same components, they are present in a different concentration and thus also the ratios of the components to one another can be altered.

BRIEF DESCRIPTION OF THE DRAWINGS

[00024] This invention is explained in greater detail below on the basis of an example. The respective drawings show:

[00025] Figure 1: A bar chart showing propylene yields of the ten best catalysts of a generation as a function and [sic; of] their increase within four generations;

[00026] Figure 2: Schematic diagram of crossing and mutation.

DETAILED DESCRIPTION OF THE INVENTION

[00027] With reference to Figure 2, it should be pointed out that the primary components listed on the left in each case are the elements used in producing the catalytic materials, where the index 1 denotes that this component is present in the catalyst, while the index 0 describes the absence of this component.

Example

[00028] Catalysts were prepared and tested with the goal of producing [sic; converting] propane to propylene by oxidation with oxygen and minimizing the resulting CO and CO₂ oxides. The course of this process included the following steps and led to the results described below.

Experimental procedure

[00029] The starting components containing the primary components of the mixed catalysts were first dissolved or suspended in water and mixed with " α -Al₂O₃ (CONDEA, particle diameter = 1.0 μ m, S_{BET} = 5 m²/g), which functioned as an inert diluent material. The volume of the solution/dispersion used per 1 g Al₂O₃ was 10 mL. The mixture was stirred for 30 minutes at 80 °C. Excess water was evaporated off while stirring at 100 °C. The remaining solid was dried at 120 °C for ten hours and calcined in air for three hours at 600 °C. The starting compounds were: NH₄VO₃ (Merck, analytical purity), Mg(NO₃)₂·4H₂O (Merck, analytical purity), H₃BO₃ (Merck, analytical purity), (NH₄)₆Mo₇O₂₄·4H₂O (Riedel de Haën, analytical purity), La(NO₃)₂·6H₂O (Merck, analytical purity), Mn(NO₃)₂·4H₂O (Merck, p. a.), Fe(NO₃)₃·9H₂O (Fluka, analytical purity), Ga(NO₃)₂·6H₂O (Alfa, 99.9 %).

[00030] The performance parameters of the catalysts were determined in U-shaped tubular reactors (I.D. = 6 mm) made of quartz and operated in parallel. To minimize the temperature

reaction temperature was 500°C in all the experiments. The reaction gas mixture consisted of propane, oxygen and nitrogen ($C_3H_8/O_2/N_2 = 3/1/6$); 0.3 g catalyst was used. The total volume flow was varied in the range of 10 to 150 mL/min (STP). On-line gas chromatography was used for analysis of the reaction gases.

Results

[00031] First step: *Production of the first generation of catalytic materials from the primary components identified*

[00032] The compositions of different catalytic materials were determined according to the random principle (see Table 1) by combining four primary components per material. The total number of materials of the first generation was 56. This number was retained in all further generations. Table 1 summarizes the compositions of the first generation catalysts.

[00033] Second step: *Parallel preparation and testing of first-generation catalytic materials*

[00034] The materials were produced according to the procedure described in the experimental section and were tested in parallel. The propylene yields obtained with the first-generation catalysts are shown in Figure 1.

[00035] Third step: *Producing the second generation based on the results of testing the first generation of catalysts*

[00036] First, 37 mixed catalysts of the second generation were produced by crossing. To do so, two mixed oxide catalysts were selected from the first generation, one of the two catalysts (catalyst A) being selected randomly while the other catalyst (catalyst B) was selected with the probability W_i which is determined by the catalytic performance parameters according to the formulation:

[00040] Most mixed catalysts which give good yields consist of V, Mg, Mo, Ga or V, Mg, Ga. Figure 2 shows that a reproducible increase in propylene yield of the most efficient catalyst of a generation is achieved from one generation to the next. The following compositions led to the best C_3H_6 yields: $V_{0.25}Mg_{0.52}Mo_{0.12}Ga_{0.11}O_x$ (first generation), $V_{0.47}Mo_{0.05}Mn_{0.27}Ga_{0.21}O_x$ (second generation), $V_{0.22}Mg_{0.47}Mo_{0.11}Ga_{0.20}O_x$ (third generation), $V_{0.27}Mg_{0.37}Mo_{0.12}Fe_{0.13}Ga_{0.11}O_x$ (fourth generation). The highest C_3H_6 yield was 9.0 % (selectivity 57.4 %).

[00041] In the compositions of the fourth generation, it is clear that even after the fourth generation, all the primary components are still represented in the generation, although the presence of components which did not lead to any significant propylene yield in the first generations is low. This is attributable to the selection principles for restructuring of the catalyst described in Patent Claim 1, said principles ensuring a higher target accuracy of the optimization process than achieved with a purely performance-oriented catalyst selection. Thus, in comparison with the method claimed according to Unexamined German Patent 198 43 242.9-41 (September 11, 1998) "Method of producing active and/or selective solid catalysts from inorganic and organometallic solids or mixture thereof" (authors M. Baerns, O. Buyevskaya, P. Claus, U. Rodemerck, D. Wolf), a higher catalyst performance is achieved in optimization with the procedure described above.

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Composition of catalytic materials of the first generation

| Cat. No. | Content/Atomic fraction | | | | | | | Ga |
|-------------|-------------------------|------|------|------|------|------|------|------|
| | V | Mg | B | Mo | La | Mn | Fe | |
| 1 | 0.24 | | | | 0.33 | | 0.15 | 0.28 |
| 2 | | 0.42 | | 0.11 | | 0.20 | 0.28 | |
| 3 | | 0.41 | 0.31 | | | | 0.05 | 0.24 |
| 4 | 0.47 | | 0.14 | | 0.27 | | | 0.12 |
| 5 | | | 0.42 | 0.29 | | 0.23 | | 0.06 |
| 6 | | 0.36 | 0.10 | | | 0.41 | 0.13 | |
| 7 | | | | 0.32 | 0.20 | 0.26 | 0.22 | |
| 8 | | 0.21 | | 0.15 | | | 0.33 | 0.32 |
| 9 | 0.16 | | | | 0.27 | 0.10 | | 0.46 |
| 10 | | 0.30 | 0.28 | 0.13 | | | 0.28 | |
| 11 | | | 0.27 | | | 0.45 | 0.06 | 0.22 |
| 12 | | | | 0.17 | 0.14 | 0.56 | 0.13 | |
| 13 | | 0.34 | | | 0.19 | 0.16 | | 0.30 |
| 14 | | 0.36 | 0.08 | | 0.25 | | 0.32 | |
| 15 | 0.44 | | | 0.11 | | 0.26 | | 0.19 |
| 16 | 0.05 | 0.30 | | | 0.41 | | | 0.24 |
| 17 | 0.10 | 0.05 | 0.44 | | | 0.41 | | |
| 18 | 0.42 | 0.40 | | | | | 0.04 | 0.14 |
| 19 | | 0.02 | | | 0.51 | 0.25 | 0.22 | |
| 20 | 0.25 | 0.52 | | 0.12 | | | | 0.11 |
| 21 | | 0.33 | | 0.31 | 0.20 | | 0.15 | |
| 22 | 0.002 | | 0.37 | | | | 0.18 | 0.45 |
| 23 | 0.08 | | | 0.49 | 0.40 | | 0.04 | |
| 24 | | 0.13 | | 0.43 | 0.14 | | | 0.29 |
| 25 | | 0.39 | | | 0.46 | | 0.04 | 0.12 |
| 26 | | 0.05 | | 0.19 | | 0.53 | 0.22 | |
| 27 | | 0.29 | | 0.24 | 0.33 | | | 0.13 |
| 28 | 0.04 | | 0.46 | 0.25 | 0.26 | | | |
| 29 | 0.05 | | | | 0.26 | 0.29 | | 0.3 |
| 30 | | | 0.32 | | | 0.09 | 0.42 | 0.18 |
| 31 | 0.005 | | | 0.42 | | | 0.17 | 0.41 |
| 32 | | | 0.42 | 0.09 | | 0.02 | | 0.47 |

Table 1 (continued)

Composition of catalytic materials of the first generation

| Cat. No. | Content/Atomic fraction | | | | | | | Ga |
|-------------|-------------------------|------|------|------|------|-------|------|------|
| | V | Mg | B | Mo | La | Mn | Fe | |
| 33 | 0.27 | 0.35 | | 0.05 | 0.34 | | | |
| 34 | 0.47 | | 0.15 | | | | 0.35 | 0.03 |
| 35 | | 0.31 | | 0.24 | 0.14 | | 0.31 | |
| 36 | 0.22 | | 0.38 | 0.13 | | 0.27 | | |
| 37 | | | 0.05 | 0.32 | 0.02 | | 0.61 | |
| 38 | 0.24 | | | | | 0.26 | | 0.27 |
| 39 | | 0.05 | | 0.45 | | 0.12 | 0.39 | |
| 40 | 0.26 | | | | 0.07 | | 0.59 | 0.08 |
| 41 | | 0.11 | 0.12 | | 0.09 | | | 0.68 |
| 42 | 0.28 | | | 0.23 | 0.3 | 0.19 | | |
| 43 | 0.05 | | 0.24 | 0.38 | | | | 0.32 |
| 44 | | | 0.41 | | 0.24 | | 0.24 | 0.12 |
| 45 | | 0.2 | | 0.24 | | 0.34 | | 0.21 |
| 46 | 0.44 | | 0.28 | | 0.03 | | | 0.24 |
| 47 | 0.25 | 0.35 | | 0.27 | | | 0.13 | |
| 48 | 0.36 | | | | | 0.3 | 0.25 | 0.09 |
| 49 | | 0.7 | 0.1 | | | 0.12 | | 0.08 |
| 50 | | | 0.22 | | 0.13 | 0.32 | | 0.33 |
| 51 | 0.27 | 0.34 | | 0.21 | | | 0.18 | |
| 52 | 0.13 | | | | 0.07 | | 0.43 | 0.37 |
| 53 | | | 0.23 | 0.21 | 0.24 | | 0.31 | |
| 54 | 0.18 | 0.2 | | | | | 0.32 | 0.3 |
| 55 | | | 0.31 | | | 0.28 | | 0.17 |
| 56 | | 0.26 | | | 0.34 | 0.004 | 0.39 | |

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Table 2

Composition of catalytic materials of the fourth generation

| Cat. No. | Content/Atomic fraction | | | | | | | Ga |
|-------------|-------------------------|------|------|------|------|------|------|------|
| | V | Mg | B | Mo | La | Mn | Fe | |
| 1 | 0.30 | | | 0.34 | | 0.36 | | |
| 2 | 0.36 | 0.22 | | 0.18 | | 0.09 | | 0.15 |
| 3 | 0.20 | 0.28 | | 0.09 | | | 0.10 | 0.32 |
| 4 | 0.21 | 0.53 | | 0.16 | | 0.10 | | |
| 5 | 0.22 | 0.47 | | 0.21 | | | | 0.10 |
| 6 | 0.27 | 0.55 | | 0.09 | | | | 0.12 |
| 7 | 0.71 | | | 0.09 | | 0.20 | | |
| 8 | 0.27 | 0.37 | | 0.12 | | | 0.13 | 0.11 |
| 9 | 0.20 | 0.28 | | 0.09 | | 0.26 | 0.10 | 0.06 |
| 10 | 0.54 | | | 0.14 | | 0.32 | | |
| 11 | 0.29 | 0.28 | | | 0.31 | | 0.03 | 0.10 |
| 12 | 0.18 | 0.25 | | 0.08 | | | 0.09 | 0.40 |
| 13 | 0.44 | | | 0.25 | | 0.13 | | 0.20 |
| 14 | 0.18 | 0.26 | | 0.19 | | | 0.10 | 0.27 |
| 15 | 0.51 | | | 0.13 | | 0.15 | | 0.21 |
| 16 | 0.52 | | | 0.24 | | | | 0.23 |
| 17 | | 0.51 | | 0.20 | | 0.29 | | |
| 18 | 0.44 | | 0.17 | | | 0.29 | 0.04 | 0.06 |
| 19 | 0.28 | | | 0.07 | | 0.07 | 0.46 | 0.12 |
| 20 | 0.13 | 0.19 | | 0.14 | | | 0.14 | 0.39 |
| 21 | 0.16 | 0.21 | | | | | 0.11 | 0.52 |
| 22 | | | 0.34 | | | 0.55 | | 0.11 |
| 23 | 0.40 | | | 0.20 | | 0.23 | | 0.17 |
| 24 | 0.21 | 0.26 | | 0.07 | | | 0.14 | 0.33 |
| 25 | 0.23 | 0.22 | | 0.45 | | | 0.02 | 0.08 |
| 26 | 0.41 | 0.25 | | 0.10 | | 0.05 | | 0.18 |
| 27 | 0.19 | 0.39 | | 0.09 | | | | 0.33 |
| 28 | 0.40 | | | 0.05 | | 0.23 | | 0.33 |

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Table 2 (continuation)

Composition of catalyst materials of the fourth generation

| Cat. No. | Content/Atomic fraction | | | | | | Ga |
|-------------|-------------------------|------|------|------|------|------|------|
| | V | Mg | B | Mo | La | Mn | Fe |
| 29 | 0.18 | 0.78 | | | | | 0.04 |
| 30 | 0.42 | 0.44 | | 0.10 | | | 0.05 |
| 31 | | 0.77 | | 0.23 | | | |
| 32 | 0.47 | | | 0.06 | | 0.27 | 0.20 |
| 33 | 0.64 | 0.30 | | | | | 0.06 |
| 34 | 0.27 | 0.34 | | 0.09 | | | 0.19 |
| 35 | 0.54 | | | 0.14 | | 0.32 | |
| 36 | 0.50 | | | | | 0.29 | 0.21 |
| 37 | 0.45 | 0.14 | | 0.11 | | 0.11 | 0.19 |
| 38 | 0.19 | 0.48 | | 0.15 | | | 0.12 |
| 39 | | 0.40 | | 0.16 | | 0.16 | 0.28 |
| 40 | 0.20 | 0.43 | | 0.10 | | | 0.22 |
| 41 | 0.29 | 0.38 | | 0.23 | | | 0.10 |
| 42 | | | | | 0.15 | | 0.85 |
| 43 | 0.29 | 0.31 | | 0.14 | | | 0.26 |
| 44 | 0.18 | 0.37 | | 0.08 | | | 0.33 |
| 45 | 0.47 | | | 0.05 | | 0.28 | 0.20 |
| 46 | 0.28 | 0.59 | | 0.07 | | | 0.06 |
| 47 | 0.16 | 0.20 | | 0.12 | 0.36 | | 0.11 |
| 48 | 0.30 | 0.39 | | 0.24 | | | 0.65 |
| 49 | 0.20 | | | 0.15 | | | |
| 50 | 0.46 | 0.49 | | | | | 0.05 |
| 51 | 0.13 | 0.67 | | 0.20 | | | |
| 52 | 0.09 | 0.21 | 0.39 | | | | 0.32 |
| 53 | 0.41 | 0.25 | | 0.10 | | 0.05 | 0.18 |
| 54 | 0.34 | 0.48 | | | | | 0.17 |
| 55 | 0.14 | 0.20 | | 0.15 | | 0.20 | 0.08 |
| 56 | 0.28 | 0.57 | | 0.13 | | | |

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Table 3

Composition of the ten best catalytic materials yielding the highest propylene yield in each generation

| <i>i</i> or <i>j</i> | Generation 1 | Generation 2 | Generation 3 | Generation 4 |
|----------------------|--|--|---|---|
| 1 | $V_{0.25}Mg_{0.52}Mo_{0.12}Ga_{0.11}O_x$ | $V_{0.47}Mo_{0.05}Mn_{0.27}Ga_{0.2}O_x$ | $V_{0.22}Mg_{0.47}Mo_{0.11}Ga_{0.2}O_x$ | $V_{0.27}Mg_{0.37}Mo_{0.12}Fe_{0.13}Ga_{0.1}O_x$ |
| 2 | $V_{0.44}Mo_{0.11}Mn_{0.26}Ga_{0.19}O_x$ | $V_{0.33}Mg_{0.33}Fe_{0.03}Ga_{0.28}O_x$ | $V_{0.3}Mg_{0.63}Ga_{0.07}O_x$ | $V_{0.29}Mg_{0.31}Mo_{0.14}Ga_{0.26}O_x$ |
| 3 | $V_{0.42}Mg_{0.4}Fe_{0.04}Ga_{0.14}O_x$ | $V_{0.32}Mo_{0.22}Mn_{0.23}Ga_{0.17}O_x$ | $V_{0.14}Mg_{0.2}Mo_{0.15}Fe_{0.08}Ga_{0.42}O_x$ | $V_{0.15}Mg_{0.39}Mo_{0.09}Ga_{0.33}O_x$ |
| 4 | $V_{0.27}Mg_{0.34}Mo_{0.21}Fe_{0.18}O_x$ | $Mg_{0.26}Mo_{0.31}Mn_{0.44}O_x$ | $V_{0.4}Mg_{0.42}Mo_{0.09}Ga_{0.09}O_x$ | $V_{0.35}Mg_{0.3}Mo_{0.2}Mn_{0.15}Ga_{0.08}O_x$ |
| 5 | $V_{0.36}Mn_{0.3}Fe_{0.25}Ga_{0.09}O_x$ | $V_{0.27}Mo_{0.19}Fe_{0.43}Ga_{0.11}O_x$ | $V_{0.39}Mg_{0.24}Mo_{0.1}Mn_{0.1}Ga_{0.17}O_x$ | $V_{0.41}Mg_{0.23}Mo_{0.1}Mn_{0.05}Ga_{0.18}O_x$ |
| 6 | $V_{0.18}Mg_{0.2}Fe_{0.32}Ga_{0.3}O_x$ | $V_{0.31}Mg_{0.39}Mo_{0.1}Fe_{0.21}O_x$ | $V_{0.24}Mg_{0.32}Mo_{0.19}Fe_{0.16}Ga_{0.08}O_x$ | $V_{0.42}Mg_{0.44}Mo_{0.1}Ga_{0.05}O_x$ |
| 7 | $V_{0.25}Mg_{0.35}Mo_{0.27}Fe_{0.13}O_x$ | $V_{0.3}Mg_{0.42}Mo_{0.13}Fe_{0.17}O_x$ | $V_{0.27}Mg_{0.38}Mo_{0.12}Fe_{0.14}Ga_{0.08}O_x$ | $V_{0.27}Mg_{0.34}Mo_{0.09}Fe_{0.19}Ga_{0.11}O_x$ |
| 8 | $B_{0.42}Mo_{0.09}Mn_{0.02}Ga_{0.47}O_x$ | $V_{0.24}La_{0.12}Ga_{0.65}O_x$ | $V_{0.53}Mg_{0.25}Fe_{0.05}Ga_{0.18}O_x$ | $V_{0.2}Mg_{0.28}Mo_{0.09}Fe_{0.1}Ga_{0.32}O_x$ |
| 9 | $V_{0.26}La_{0.07}Fe_{0.59}Ga_{0.08}O_x$ | $V_{0.52}Mo_{0.13}Mn_{0.13}Ga_{0.22}O_x$ | $V_{0.55}Mo_{0.06}Mn_{0.16}Ga_{0.23}O_x$ | $V_{0.47}Mg_{0.03}Mn_{0.28}Ga_{0.2}O_x$ |
| 10 | $V_{0.47}B_{0.15}Fe_{0.35}Ga_{0.03}O_x$ | $V_{0.27}Mg_{0.57}Mo_{0.13}Ga_{0.06}O_x$ | $V_{0.23}Mg_{0.59}Mo_{0.18}O_x$ | $V_{0.18}Mg_{0.28}Mo_{0.13}Fe_{0.1}Ga_{0.27}O_x$ |